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MODELLING THERMODYNAMICS OF ALLOYS FOR FUSION APPLICATION .

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OBJECTIVE

This research has two main objectives:

- The development of computational tools to evaluate alloy properties, using the information contained in thermodynamic functions. We aim at improving the ability of classical potentials to account for complex alloy behavior, and
- The application of these tools to predict properties of alloys under irradiation.

SUMMARY

Atomistic simulations of alloys at the empirical level face the challenge of correctly modeling basic thermodynamic properties. In the periods reported previously we develop a methodology to generalize many-body classic potentials to incorporate complex formation energy curves. Application to Fe-Cr allows us to predict the implications of the ab initio results of formation energy on the phase diagram of this alloy and to get a detailed insight into the processes leading to precipitation of α' phase under irradiation. In particular in this period we report on the consequences of the negative heat of formation at low Cr composition on the short range order SRO existing in the α phase. We elaborate a simple description of SRO on a two phase alloy and compare the predictions with experiments. We provide a key to rationalize a diversity of experiments on SRO versus annealing time or irradiation dose.

PROGRESS AND STATUS

Two main activities were developed in the period covered by this report.

- 1- **Short-range order (SRO) in Fe-rich Fe-Cr alloys** was investigated by means of atomistic off-lattice Monte Carlo simulations in the semi-grand canonical ensemble using classical interatomic potentials. The parameters defined by Cowley are used to quantify the SRO. In agreement with experiments we observe a strong ordering tendency in the Cr distribution at low Cr concentrations $c \sim < 5\%$ as manifested in negative values of the SRO parameters. For intermediate Cr concentrations, $5\% < c < 15\%$, the average SRO parameter for the α -phase goes through a minimum and eventually approaches zero indicating the formation of a random solid solution. However, in this concentration range the system is actually in a two-phase region. In thermodynamic equilibrium the SRO parameter measured over the entire system therefore comprises the contributions from both the α and α' phases. Taking into account these contributions we were able to quantitatively reproduce the experimental results and interpret their physical implications.
- 2- **Impurity segregation at grain boundaries in polycrystalline materials.** We applied a novel approach to computationally model the problem of impurity segregation at grain boundaries in polycrystalline materials. It is based on the parallel Monte Carlo algorithm that places the impurities according to the local chemical potential for the species, following the thermodynamic driving force for segregation. We described this code in previous reports. We report now on a test case of a CuFe alloy and study the role played by Fe impurities in nanocrystalline Cu (nanocrystalline because it is a way to explore many different grain boundaries in a single simulation) from three different perspectives.

i- We found a strong decrease in grain boundary mobility resulting in an enhancement of the stability of nanophase grain boundaries upon annealing. ii- Virtual tensile tests of samples with and without impurities reveals a hardness that is unaffected by the presence of the Fe impurities. We interpret the striking difference between these two results in terms of impurity dragging versus sliding, and derive general conclusions regarding hardness at the nanoscale in dirty materials. iii- Grain boundary cohesion, in turn, is studied via spall resistance to tensile stress produced by simulated laser irradiation, that shows enhanced grain boundary cohesion in the case of the sample bearing impurities. All these examples help us preparing the field for the study of Cr segregation, a problem whose main characteristics were already reported in the previous period.

In what follows we briefly describe the first of these achievements.

Short-range order (SRO) in Fe-rich Fe-Cr alloys. Iron-chromium steels are used in reactor environments because of their swelling and corrosion resistance as well as their high-temperature creep resistance and hardness. The precise origin of many of these beneficial features is still uncertain. Creep resistance is customarily associated with the presence of small α' precipitates, while embrittlement has been related to the presence of larger α' precipitates. The α and α' phases are the Fe-rich and Cr-rich solid solutions into which the body-centered cubic (bcc) phase of the alloy decomposes at temperatures below about 1000 K. The standard phase diagram for this alloy has been assessed using the CALPHAD methodology. In this approach the mixture has been assumed to behave like a standard segregating mixture at temperatures below the existence range of the σ -phase. There are, however, well known anomalies in the location of the solvus in annealed and irradiated samples which suggest a more complex behavior. A breakthrough in the understanding of the microstructure of these alloys was made through neutron diffraction measurements which showed 1- negative Cowley short-range order (SRO) parameters at small Cr concentrations indicating strong short-range ordering of Cr atoms, and 2- an inversion of the sign of these parameters with increasing Cr concentration suggesting the formation of α' precipitates. The implications of these discoveries for the interpretation of enhanced creep resistance and embrittlement are apparent since SRO is known to affect the mobility of dislocations, and precipitation plays a role in intergranular cracking. Nonetheless the understanding of the atomistic details of the complex behavior of this alloy is still incomplete. This situation has motivated a number of recent first principles studies which addressed the energetics of this system. These calculations revealed a change of sign in the heat of formation of the solution from the negative to the positive side as the Cr concentration increases above 10%. Detailed analysis of the origin of this anomaly showed that, while the heat of solution of a Cr impurity in Fe is large and negative, magnetic frustration leads to a strong Cr-Cr repulsion, causing the heat of formation to assume large positive values as the Cr content increases. These advances in the improved understanding of the energetics of Fe-Cr alloys have provided the basis for the development of accurate interatomic potential models, which enable large scale simulations of the microstructural evolution. Two approaches were developed known as the two band model and the composition dependent model, which both address the complex shape of the heat of formation curve at 0K as determined from the aforementioned first-principles calculations. Using our composition dependent model, we recently studied the implications of the change in sign of the heat of formation on the thermodynamic behavior at finite temperatures and proposed a modified phase diagram for Fe-Cr in the region of low Cr content and temperatures below the range of existence of the σ -phase. In fact compared to the CALPHAD assessment, which is based on the assumption of a standard segregating binary mixture, a better agreement with the experimental location of the solvus was obtained.

From our viewpoint, three aspects render the study of SRO in Fe-Cr alloys particularly interesting: (1) Experimental measurements of SRO parameters of heterogeneous systems (such as mixtures of α and α') provide only compound quantities equivalent to averages over the entire sample. (2) In Fe-Cr this situation is further complicated by the ordering tendency of the system at low Cr concentrations. (3) The recent advances in the development of Fe-Cr interatomic

potentials and the availability of suitable simulation techniques (semi-grand canonical Monte Carlo) provide the possibility to explore the atomistic details of these processes. Thereby, we are able to resolve the contributions to the experimentally measured quantities and understand the microscopic behavior of the material. In this paper, we discuss the evolution of SRO in a mixture of two phases and the influence of the kinetics of alloy decomposition on the time evolution of the SRO parameters.

Figure 1 shows the equilibrium Cr concentration which is established for a given chemical potential and temperature. The curves can be well fit assuming a regular solution on temperature, as shown by the lines in Fig.1.

$$\Delta\mu = \Delta\mu^0 + \Omega(1 - c_{Cr})^2 + k_B T \ln c_{Cr} \quad (1)$$

The concentration range shown in Fig. 1 slightly exceeds the thermodynamic equilibrium solubility as given by the phase diagram of this model (see our previous report). The system can thus be driven to some extent into the two-phase region without precipitation taking place during the course of the simulation, which is a natural consequence of a small chemical driving force, short simulation time, and/or small sample size combined with the fact that the transition has a nucleation barrier.

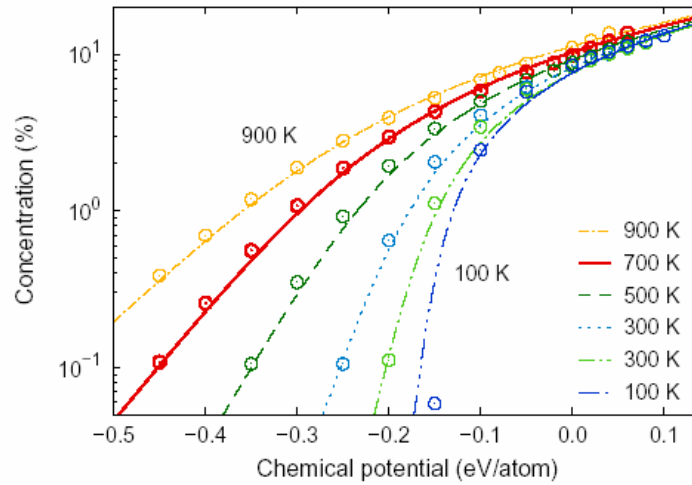


Figure 1: Relation between chemical potential and Cr concentration in α -Fe. The data points were obtained by simulation. The lines are fits to equation 1

The SRO parameters were obtained by averaging over all configurations along the Markov chain (for a given chemical potential and temperature) for which the α phase encompassed the entire sample (single phase system). The results for the bcc SRO parameter are shown in Fig. 2. Several observations can be made: For smaller concentrations the SRO becomes more negative with increasing Cr concentration. With decreasing temperature the curves approach the theoretical lower limit for the SRO parameter (dashed line in Fig. 2). For larger concentrations the SRO parameter reaches a minimum between 8 and 12% Cr, the location of which is only weakly dependent on temperature (very much unlike the solubility limit).

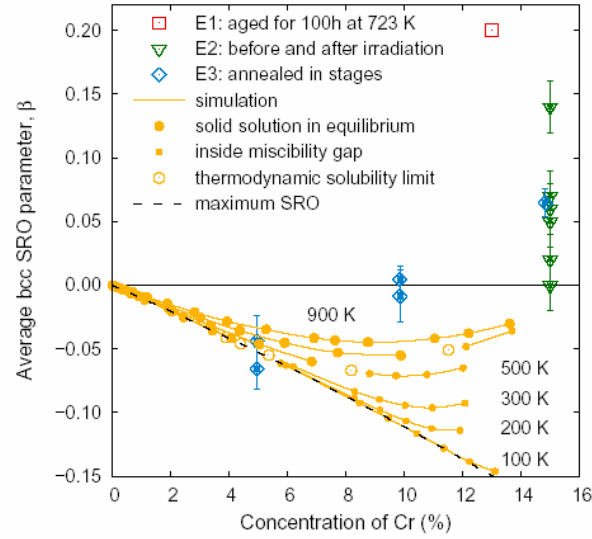


Figure 2: Dependence of the short-range order parameter on the total Cr concentration. Circles show simulation data. Solid lines serve as guide to the eyes. The dashed line represents the maximum possible order. E1: experimental data from Ref. 20; E2: experimental data from Ref. 21; E3: experimental data from Mirebeau, M. Hennion, and G. Parette, *Phys. Rev. Lett.* 53, 687 (1984).

Figure 3 shows the number distribution of SRO parameters obtained by averaging over every Cr atom in the sample after 1100 MC steps per atom which is a representative configuration for the Fe-rich homogeneous solid solution (pure α -phase). There is one pronounced peak on the negative side equivalent to the SRO of the α phase. Note that the range of SRO parameter also includes some positive values. This is related to the saturation of the α -phase which in equilibrium at this temperature would contain only about 8.2% Cr. For further illustration the configuration is shown in Fig. 4(a) clearly indicating the absence of precipitation.

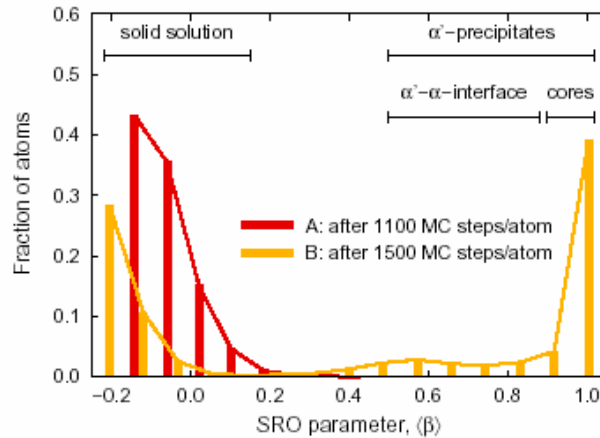


Figure 3: Number distribution of SRO parameter before (A) and after (B) the formation of super-critically sized α' -precipitates. The corresponding configurations are shown in Fig. 5.

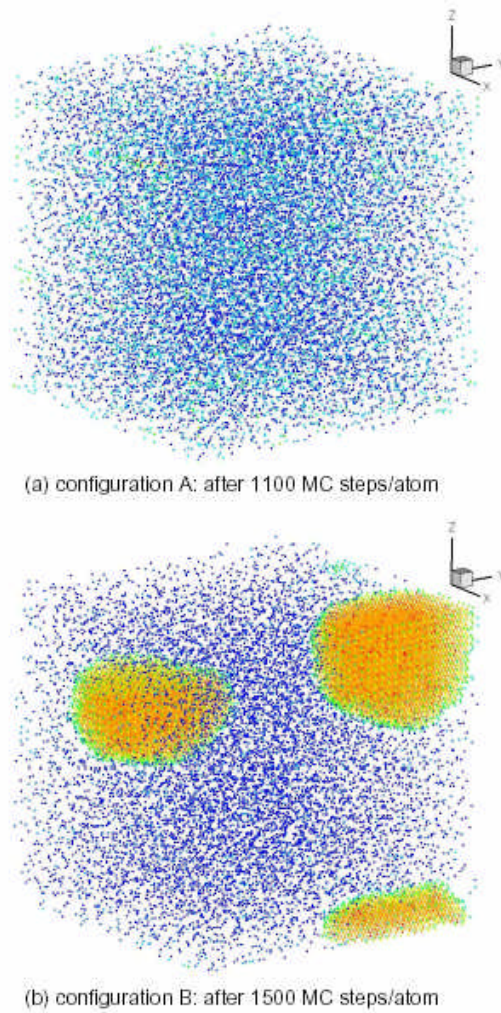


Figure 4: Atomic configurations before (a) and after (b) the formation of super-critical α' precipitate. Only Cr atoms are shown with a color coding based on their SRO parameter: blue/green: negative or small positive SRO parameter (Fe-rich solid solution, α phase), yellow/red: positive SRO parameter (α' -precipitates, α - α' -interface).

Continuing with the simulation we observe the appearance of the precipitated α' phase, and the SRO parameter histogram shows two distinct peaks (See Fig 3B), one at about -0.02, characteristic of the α phase, and one at about 1, characteristic of the α' phase. Figure 4B shows the microstructure corresponding to this situation. Clearly, the average SRO parameter is the result of a combination of these two peaks in the bimodal histogram.

The results presented above demonstrate that particular care must be exercised when interpreting the SRO parameter in the case of a two-phase mixture. While the average SRO parameter for Cr atoms in the α phase is typically small and negative, the SRO parameter for Cr precipitates is close to one. Since experimentally the SRO is obtained over the entire sample, the measured value is an average over all types of local short-range order. This average is the weighted sum of the contributions from the α and α' phases as well as the α/α' interface.

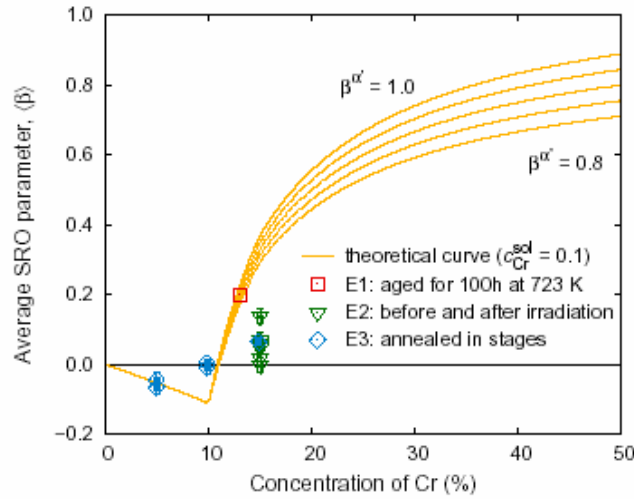


Figure 5: Theoretical prediction for the average SRO parameter. Experimental references as given in the caption of Fig. 2.

The consequence of these observations is that the sample-averaged SRO shows a composition dependence as shown in Fig 5, together with some experimental results. We do not give here the details on how these curves are obtained, but just say that they are the consequence of this simple observation that in an heterogeneous sample, the measured SRO parameter is the weighted average of the SRO in each phase. This analysis provided as with a key to interpret a series of experimental results.

In work has been submitted for publication to PRB and it can be summarized as follows: We have investigated the short-range order (SRO) in Fe-rich Fe-Cr alloys using atomistic simulations based on an empirical potential description of the alloy. For low temperatures and small concentrations the SRO in the α phase is found to be close to the theoretical maximum possible SRO. As temperature increases SRO is reduced due to entropic effects. For somewhat larger Cr concentrations the SRO curves go through a minimum and subsequently approach zero. This behavior reflects the competition between energy induced ordering and entropy-driven randomization. In the two-phase region the experimentally assessed SRO parameter is a mixture of both the SRO in the α phase and the α' precipitates. The simulations show that the two contributions can be clearly separated. When using a weighted average of these contributions the average SRO parameter is predicted as a function of concentration in good agreement with experiment. This model has also been used to investigate the effect of temperature on the SRO parameter which shows the temperature dependence of the solubility of Cr in Fe to be the dominating factor. The results reported here are anticipated to support future research in at least two aspects: (1) As indicated in the introduction the SRO affects the mobility of dislocations. The present paper therefore constitutes a basis for a detailed atomistic study of the mobility of dislocations in Fe-Cr alloys. The present paper clarifies the contributions to the average SRO parameter in a two-phase system and introduces a simple predictive model. It thereby provides a better understanding of previous experimental results and provides the basis for a more elaborate interpretation of future experiments.

Impurity segregation at grain boundaries in polycrystalline materials

In the last few years of work in this project we have developed the grounds to model real alloys using computer simulations. The path followed involves the development of model and tools. At the present stage of our work, we are able to explore a diversity of relevant problems in metallurgy, in particular those related to impurities / solute segregation at defects like grain

boundaries. As a first application of our tools to this problem, we studied nanophase 'dirty' materials, i. e. a large collection of grain boundaries with a small amount of solute or impurities. We just submitted a paper in which we present this novel computational approach to model the problem of segregation at grain boundaries, whose content can be summarized as follows: using a new parallel Monte Carlo code in the transmutation ensemble with displacements and a thermodynamically assessed classical potential for the alloy of interest, we have been able to prepare nanocrystalline samples showing heterogeneous precipitation of an insoluble impurity at grain boundaries. This result is in agreement with experimental evidence of the segregation of Fe impurities to Cu grain boundaries reported by Bernardini and coworkers [30]. Our methodology allows us to construct realistic microstructures of a highly non ideal binary alloy thus enabling quantitative studies of impurity effects on several relevant properties. Pure and dirty samples have been subjected to different tests: aging, tensile deformation and fracture resistance. Our simulations show that a small concentration of insoluble impurities that precipitate at GB's are capable of causing drastic reductions in GB mobilities, increase cohesion, and have negligible effects on its mechanical properties. We interpret the results in terms of different atomic motion in the grain boundary region. Grain boundary sliding or motion of the grains relative to each other in a direction parallel to the grain boundary does not require mass transport to maintain the preferred equilibrium partition of the impurities between grain boundary and bulk. Sliding can occur through atomic shuffles not involving diffusion of the impurity. On the other hand, grain boundary migration and grain growth imply motion of the grain boundaries perpendicular to the grain boundary plane and require mass transport of the impurity together with GB motion in order to maintain the equilibrium segregation ratio. This distinction can be extremely important in the effects of impurities in the mechanical and annealing behavior of nanocrystalline materials. Our results show that grain boundary sliding and mobility can be affected in dramatically different ways by the addition of impurities. These two processes are controlled by different characteristics of the impurity. The effects on grain boundary mobility are controlled by the tendency of the impurity to segregate to the grain boundary. On the other hand, one may speculate that grain boundary sliding is controlled by the effect of the impurity on the free volume of the grain boundary. In our case, there is a negligible effect of the impurities on the free volume in the boundary region because of the similar sizes of the Fe and Cu atoms. Grain boundary embrittlement can be controlled by both size and chemical effects [29] and can be influenced by the chemical part, even in the absence of size effects. Our newly developed tools allowed us to explore the important process of heterogeneous impurity segregation at GB and its effect on GB stability and plasticity, opening in this way the possibility of modeling more realistic -dirty- samples. Our technique will allow the engineering of interfaces for desired grain boundary mobility and mechanical response, something that is crucial for a number of applications such as building better first wall materials for Magnetic Confinement Fusion or targets for the National Ignition Facility which requires reduced GB motion, and also improved materials for the new generation of nuclear reactors, where GB of nanophase materials could act as sinks for radiation-induced defects.

Conclusion:

In the period reported here, several applications of the model developed previously have been completed and show novel properties of this alloy. These results are being published and presented in numerous conferences, many of them as Invited Talks.

Publications

A. Caro, M. Caro, P. Klaver, B. Sadigh, E.M. Lopasso, and S.G. Srinivasan, "The Computational Modeling of Alloys at the Atomic Scale: From Ab Initio and Thermodynamics to Radiation-Induced Heterogeneous Precipitation", *Journal of Minerals, Metals and Materials (JOM)*, USA, April 2007, p52-57.

P. Erhart, A. Caro, M. Serrano de Caro, B. Sadigh, "Short-range order and precipitation in Fe-rich Fe-Cr alloys", submitted to Phys. Rev. B

A. Caro, D. Farkas, E. M. Bringa, G. H. Gilmer, and L. A. Zepeda-Ruiz. "Mobility and mechanical response of dirty interfaces in nanocrystalline Cu". Submitted to Phys. Rev. B

C. Jiang, S. G. Srinivasan, A. Caro, and S. A. Maloy. "Structural and elastic properties of Cementite from first-principles calculations". Submitted to Phys. Rev. B

Conference Presentations

M. Caro, A. Caro, P. Erhart, "Heterogeneous Precipitation in FeCu", poster presentation M&C+SNA 2007, April 15-19, 2007, Monterey, CA, US.

M. Caro, P. Klaver, H. Dogo, R. Till, A. Caro, "Point Defects and Precipitation in FeCr Alloys", 2007 TMS Conference, Orlando, Florida, US, Feb. 25 - Mar. 1 (2007) UCRL-PRES-228451.

M. Caro, A. Caro "Heterogeneous precipitation of Cu in Fe-Cu alloys", International Group on Radiation Damage Mechanism, IGRDM-13, 15-20 October 2006, Tsukuba, Japan, UCRL-CONF-225781

M. Caro, J. Marian, E. Martinez, A. Caro, E.M. Lopasso, D.A. Crowson, A. Arsenlis, M. Victoria, J. M. Perlado, "Critical Issues on Materials for Gen-IV Reactors", poster presentation American Nuclear Society ANS Annual Meeting in Reno, Nevada (June 4-8, 2006), UCRL-POST-221431.